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Assembled Monolayers Depends upon the Roughness of the Substrate and the Orientation of the Terminal Moiety

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Odd–Even Effect in the Hydrophobicity of *n*-Alkanethiolate Self-Assembled Monolayers Depends upon the Roughness of the Substrate and the Orientation of the Terminal Moiety

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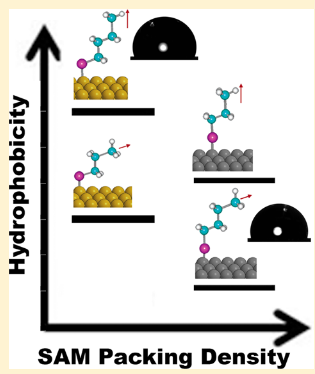
Supporting Information

ABSTRACT: The origin of the odd–even effect in properties of self-assembled monolayers (SAMs) and/or technologies derived from them is poorly understood. We report that hydrophobicity and, hence, surface wetting of SAMs are dominated by the nature of the substrate (surface roughness and identity) and SAM tilt angle, which influences surface dipoles/orientation of the terminal moiety. We measured static contact angles (θ_s) made by water droplets on *n*-alkanethiolate SAMs with an odd (SAM^O) or even (SAM^E) number of carbons (average θ_s range of 105.8–112.1°). When SAMs were fabricated on smooth "template-stripped" metal (M^{TS}) surfaces [root-mean-square (rms) roughness = 0.36 ± 0.01 nm for Au^{TS} and 0.60 ± 0.04 nm for Ag^{TS}], the odd–even effect, characterized by a zigzag oscillation in values of θ_s, was observed. We, however, did not observe the same effect with rougher "as-deposited" (M^{AD}) surfaces (rms roughness = 2.27 ± 0.16 nm for Au^{AD} and 5.13 ± 0.22 nm for Ag^{AD}). The odd–even effect in hydrophobicity inverts when the substrate changes from Au^{TS} (higher θ_s for SAM^E than SAM^O, with average $\Delta\theta_{s\,|n-(n+1)|} \approx 3°$) to Ag^{TS} (higher θ_s for SAM^O than SAM^E, with average $\Delta\theta_{s\,|n-(n+1)|} \approx 2°$). A comparison of hydrophobicity across Ag^{TS} and Au^{TS} showed a statistically significant difference (Student's *t* test) between SAM^E ($\Delta\theta_{s\,|\mathrm{Ag\ evens-Au\ evens}|} \approx 5°$; $p < 0.01$) but failed to show statistically significant differences on SAM^O ($\Delta\theta_{s\,|\mathrm{Ag\ odds-Au\ odds}|} \approx 1°$; $p > 0.1$). From these results, we deduce that the roughness of the metal substrate (from comparison of M^{AD} versus M^{TS}) and orientation of the terminal $-CH_2CH_3$ (by comparing SAM^E and SAM^O on Au^{TS} versus Ag^{TS}) play major roles in the hydrophobicity and, by extension, general wetting properties of *n*-alkanethiolate SAMs.



INTRODUCTION

The odd–even effect is a widely observed phenomenon across many disciplines that include physics, chemistry, materials science, and biology.[1−19] The odd–even effect describes an alternation in structure and/or property of an object depending upon whether there are odd or even numbers of a basic unit. In self-assembled monolayers (SAMs), the structural unit is often the number of non-hydrogen atoms, excluding the anchoring headgroup, present in the molecule that make up the monolayer (CH_2 for hydrocarbons). Understanding the odd–even effect has technological implications in the design and development of SAM-based technologies, such as molecular tunneling junctions, field-effect transistors, and molecular diodes, among many others.

To design and develop technology based on SAMs, we first sought to understand the odd–even effect in simple SAMs on Au and Ag, those derived from *n*-alkanethiolates of medium-chain length (C_9–C_{16}). Medium-chain-length monolayers are known to be well-ordered and liquid-like, and they have been employed as model systems in several studies. Although several reports have consistently shown the odd–even effect in contact angles with liquids that wet *n*-alkanethiolate SAMs, there is no clear evidence of the odd–even effect in their hydrophobicity. Figure 1a gives a summary of previously reported contact angle measurements for water on *n*-alkanethiolate SAMs that are relevant to the current study. Porter and co-workers reported an odd–even effect in hydrophobicity of *n*-alkanethiolate SAMs on Ag by measuring advancing contact angles, θ^{adv} (panel i of Figure 1a). The data by Porter and co-workers, however, were

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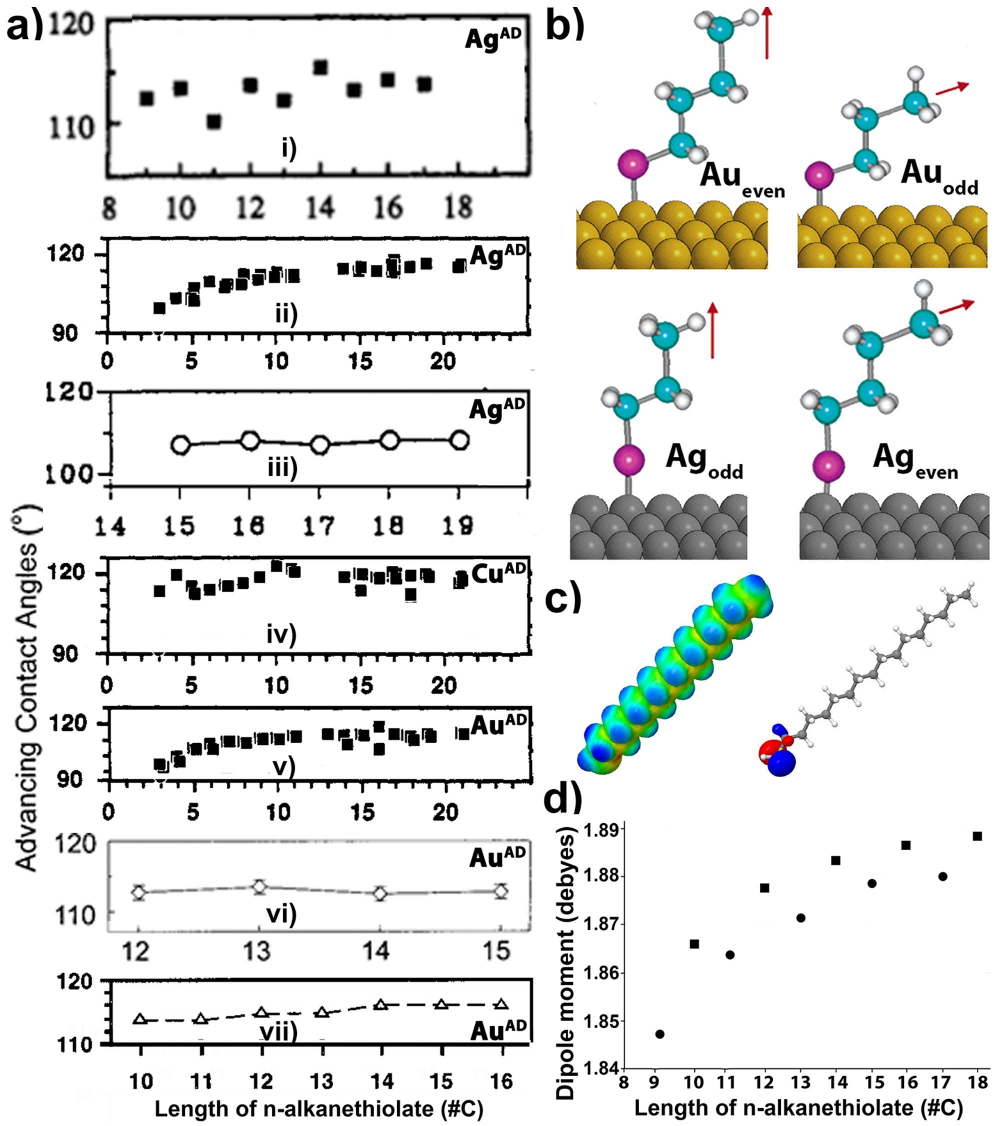

Figure 1. Summary of the structure and property relevant to the wetting properties of SAMs. (a) Hydrophobicity of *n*-alkanethiolate SAMs as captured through values of advancing contact angles formed between the SAM and a drop of water as reported by (i) Porter and co-workers,[14] (ii, iv, and v) Whitesides and co-workers,[20] (iii) Tao and Lee,[21] (vi) Colorado and Lee and Lee et al.,[22,23] and (vii) Graupe et al. and Miura et al.[24,25] on either Ag, Cu, or Au. All previous studies were performed on "as-deposited" surfaces. (b) Schematic illustration of the structural effect of the SAM tilt angle, because of change in the substrate, on the tilt and orientation of the terminal moiety (surface dipole) of *n*-alkanethiol monolayers on metal surfaces based on current generalized models of bonding and monolayer tilts angles. Orientation of the terminal moiety inverts with the change of the substrate; SAM^E on Au orients like SAM^O on Ag and vice versa. (c) Theoretically optimized electrostatic potential map and frontier orbital localization in *n*-alkanethiols as reported by Vogt.[26] (d) Calculated surface normal dipole moments for *n*-alkanethiols bound on a metal show a significantly indifferent ($\Delta D_{|n-(n-1)|} \approx 0.001$) but visible odd−even oscillation.[26] Graphs in panel a are reprinted with permission from (i) ref 14, Copyright 1991 American Chemical Society, (ii, iv, and v) ref 20, Copyright 1991 American Chemical Society, (iii) ref 21, Copyright 1994 Elsevier, (vi) ref 23, Copyright 2001 American Cheical Society, and (vii) ref 24, Copyright 1999 American Chemical Society.

inconsistent with other reports that followed (Figure 1a) and did not include statistical evaluation of the data.

■ HYDROPHOBICITY OF *N*-ALKANETHIOLATE SAMS

Previous studies on hydrophobicity of *n*-alkanethiolate SAMs, as captured in the contact angle formed between the SAM and a water droplet (θ_{adv}) on either Ag or Au, are not conclusive with regard to the presence or absence of an odd−even effect (Figure 1a).[14,22,24,25,27−30] Two of the initial studies by Laibinis et al. (Whitesides' group)[20] and Walczak et al. (Porter's group)[14] are in disagreement: the former observing an odd−even oscillation in the values of the advancing contact angle, θ_s^{adv}, while the former did not. Other studies that followed did not support the presence of an odd−even effect in the hydrophobicity of *n*-alkanethiolate SAMs.[21−25,27−29,31−33] The odd−even effect was, however, observed with liquids that wet the SAM ($\theta_s <$ 90) or when the thiol had a different terminal moiety besides $-CH_2CH_3$, for example, a terminal $-CH_2CF_3$. These CF_3-terminated *n*-alkanethiols have a larger dipole moment and interact more strongly with a relatively weak dipole, such as that in water, and this is enough to overcome surface roughness effects, giving rise to a measurable odd−even effect.[9] On the basis of the smoothness and uniformity of surfaces used in Porter's and Whitesides' work, which were largely limited by the state-of-the-art fabrication of metal films, it is surprising that Porter and co-workers observed an odd−even effect in $-CH_2CH_3$-terminated *n*-alkanethiols. The presence of an odd−even effect was deduced from a zigzag oscillation in the contact angles but was not subjected to statistical scrutiny. In these earlier studies, there was no mention of replication, data variances, or statistical evaluation.

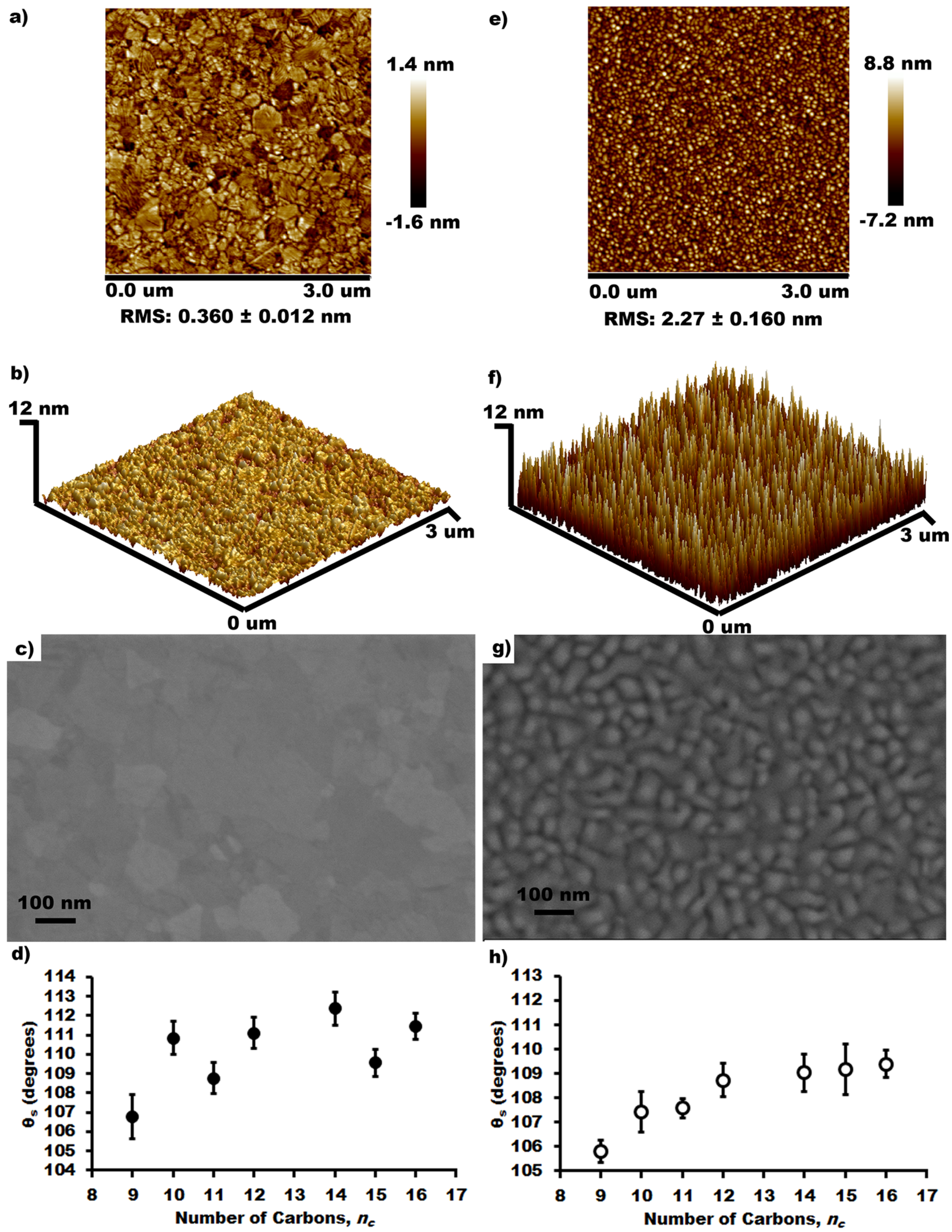

Figure 2. Surface roughness and contact angles observed with Au surfaces. AFM images of the Au^{TS} surface: (a) two-dimensional (2D) view and (b) tilted three-dimensional (3D) view of a 3 × 3 μm surface. (e and f) Similar images for the Au^{AD} surfaces. (c and d) Surface roughness and polycrystallinity were confirmed by SEM. Static contact angles formed by a drop of water on *n*-alkanethiolate SAMs formed on (d) Au^{TS} and (h) Au^{AD}, showing an odd–even effect only for the smoother surface.

With the importance of SAMs as a general platform in many technologies, this gap and inconsistency in one of the most basic properties of the SAMs ought to be addressed.

Current models of an ideal SAM (on an atomically flat surface and molecules in an all *trans*-extended conformation with no gauche rotation) suggest that an odd–even effect in wetting or other interface-dependent properties of a SAM should be expected (Figure 1b). Theoretical evaluation of the electrostatic potential maps and frontier orbital localization by Vogt[26] does not indicate any significant electronic perturbation of molecules upon bonding to the metal that could significantly influence the interface to have a major effect and, hence, warrant significant consideration (Figure 1c).[34] Optimized molecular dipole moments along the surface normal for Ag-based SAMs show a small zigzag oscillation (~0.01 D) between the odd and even *n*-alkanethiols (Figure 1d). This difference was attributed to the change in the orientation of the terminal moiety relative to the surface and has previously been implicated as a possible origin of the odd–even effect, albeit with fluorinated SAMs.[26]

We believe that the odd–even effect in SAMs, such as the zigzag oscillation in the surface normal dipole, should invert with the change of the substrate from Ag to Au and vice versa based on the known structures of SAMs on these surfaces (Figure 1b). Because odd–even effects have recently been observed in studies of charge transport by tunneling using physisorbed liquid top electrodes, we hypothesized

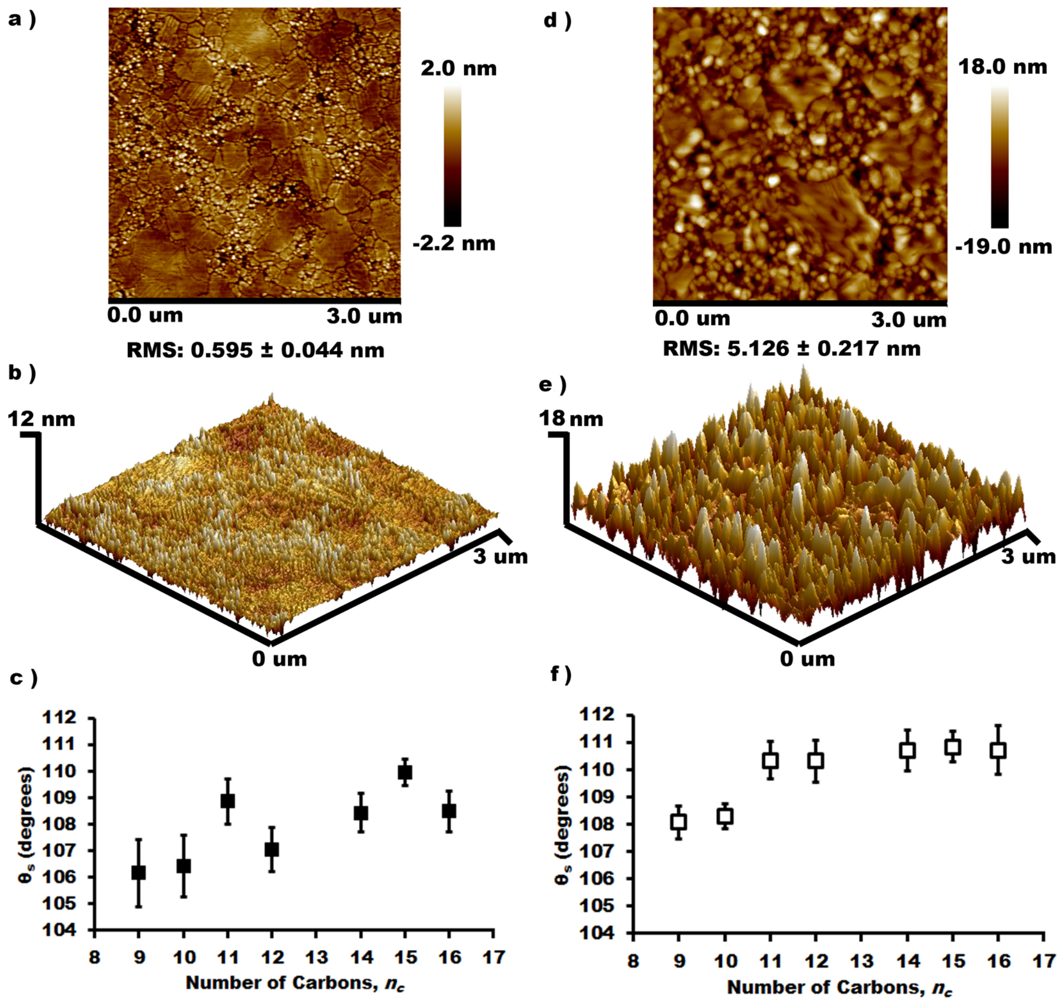

Figure 3. Surface roughness and contact angles obtained from Ag surfaces. AFM images of the Ag^{TS} surface: (a) 2D view and, (b) tilted 3D view of a 3×3 μm surface. (d and e) Similar images for the Ag^{AD} surfaces. Static contact angles formed by 5 μL of water on *n*-alkanethiolate SAMs formed on (c) Ag^{TS} and (f) Ag^{AD}, showing an odd−even effect only for the smoother surface.

that a similar statistically significant odd−even effect should be observed in the hydrophobicity of *n*-alkanethiolate SAMs. In such a case, the effect of the orientation of the terminal group and molecular packing density on the surface properties of the SAM can be deduced. These results would have consequences in application of SAMs, especially in predicting the influence of surface properties on the rate of charge injection in tunneling junctions.

■ RESULTS AND DISCUSSION

All surfaces were purchased from Substrata, Inc. and were either used as received (M^{AD}) or template-stripped (M^{TS}) as previously described.[11,19,35,36] Panels a and e of Figure 2 show atomic force microscopy (AFM) analysis of Au^{TS} [root-mean-square (rms) roughness of 0.36 ± 0.01 nm] and Au^{AD} (rms roughness of 2.27 ± 0.16 nm) surfaces. The observed roughness data are comparable to those previously observed by others.[37,38] Average rms roughness values were obtained from at least seven substrates with 10 measurements from each substrate. Generally, Au^{TS} surfaces have lower rms roughness and large grain sizes separated by shallow grain boundaries (panels a and b of Figure 2), making them ideal for the study of SAMs. On the other hand, Au^{AD} surfaces, which dominated earlier studies on wetting properties of SAMs, have large rms roughness, small grain sizes, and large grain boundaries (panels e and f of Figure 2). The differences in roughness between the two surfaces were confirmed by scanning electron microscopy (SEM), which also suggests that the surfaces could be polycrystalline (panels c and g of Figure 2).

Observation of the Odd−Even Effect Depends upon Surface Roughness. The Au^{TS} and Au^{AD} surfaces were then used to form *n*-alkanethiolate $[S(CH_2)_nH$, where $n = 8−16$, except for 13] SAMs as previously described.[11,19] When we formed *n*-alkanethiolate SAMs on Au^{TS} and measured their static contact angles with water, θ_s, we observed that SAM^E gave higher θ_s than analogous SAM^O (Figure 2d), with a characteristic zigzag oscillation with an increase in the molecular length. The data were found to be statistically significant different with a 99% confidence level using Student's *t* test ($p < 0.01$). We also observed that, as previously observed by Laibinis et al.,[20] there is a slight but gradual increase in θ_s with an increase in the molecular length [from C_9 (107.7° ± 0.7°) to C_{16} (112° ± 0.5°)]. When SAMs were formed on the rougher "as-deposited" (Au^{AD}) surfaces, there is no oscillation in θ_s between the odds and evens but the gradual increase in contact angles from C_9 (105.8° ± 0.5°) to C_{16} (109° ± 0.6°) is observed. The difference in θ_s between the shorter and longer SAMs can be attributed to the SAM becoming more rigid, giving the surface a better defined interface, or, in the case of the rough surface, the SAM starting to dictate the nature of the

Table 1. Summary of Static Contact Angles, θ_s (deg), Formed from *n*-Alkanethiolate SAMs Formed on Template-Stripped and As-Deposited Metal Surfaces

alkanethiol (number of C)	contact angle, θ_s (deg)			
	Au^{TS}	Au^{AD}	Ag^{TS}	Ag^{AD}
9	107.7 ± 0.7	105.8 ± 0.4	106.4 ± 0.9	108.1 ± 0.6
10	110.8 ± 0.7	107.4 ± 0.8	106.2 ± 1.3	108.3 ± 0.5
11	108.1 ± 0.8	107.5 ± 0.4	109 ± 0.7	110.4 ± 0.7
12	110.7 ± 0.6	108.6 ± 0.5	106.6 ± 0.8	110.3 ± 0.8
14	112.1 ± 0.9	108.9 ± 0.8	108.5 ± 0.5	110.7 ± 0.8
15	108.5 ± 0.9	108.4 ± 1	110.2 ± 0.8	110.8 ± 0.6
16	112.0 ± 0.5	109.3 ± 0.6	108.4 ± 0.7	110.7 ± 0.9

interface formed between the SAM and water rather than being dominated by the roughness of the metal substrate. Average contact angles derived from the Au^{AD} surface are slightly lower, although not a statistically significant difference, than those derived from analogous SAMs on Au^{TS} surfaces (average $\theta_s|\Delta Au^{TS} - Au^{AD}| \approx 1.3°$). From the study of wetting between the two surfaces, we can infer that an odd−even effect exists in the hydrophobicity of SAMs formed on the ultraflat Au^{TS} surface but not on the rougher Au^{AD} surface.

Jabbarzadeh and co-workers,[39] through theoretical simulation, have shown that hydrated SAM^E gives a lower coefficient of friction than analogous SAM^O on Au(111). In simulated high-pressure environments, water penetrates deeper into SAM^O than in the analogous SAM^E. On the basis of the data above, we can infer that this behavior could be driven, in part, by the fact that water wets SAM^O on Au^{TS} (lower θ_s) better than SAM^E. Because wetting is an interface phenomenon, the lower contact angle observed with SAM^O on Au^{TS} implies that water adheres better (spreads) on these surfaces than on the analogous SAM^E. Hydrophobicity is related to the work of adhesion, W_{adh}, which is related to the interfacial surface energy by the general rule $W_{adh} \approx 2\gamma_{int}$ for non-wetting surfaces according to the Young−Dupre equation (eq 1).[40] We can, therefore, infer that the spreading parameter, S, and γ_{int} are different for SAM^O and SAM^E.

$$W_{adh} = \gamma(1 - \cos\theta) \tag{1}$$

This premise, that the interface parameters S and γ_{int} are different, would imply that inverting the orientation of the surface-exposed moiety, in our case, $-CH_2CH_3$, would lead to an analogous inversion in S and γ_{int}, assuming that everything else remains the same. This inversion in surface dipoles or terminal group orientation can be achieved by changing the substrate from Au^{TS} to Ag^{TS} (Figure 1b).[41] It is, however, well-known that SAMs on Ag $[(\sqrt{7} \times \sqrt{7})R19.1°]$ are more densely packed than those on Au $[(\sqrt{3} \times \sqrt{3})R30°]$, where the surface area per adsorbed molecule is 29% larger,[41,42] hence, the need to devolve the effect of the packing density from changes as a result of surface dipoles, which is the result of the orientation of the terminal group. Figure 1b shows that, for SAM^E on Au, the surface-exposed $-CH_2CH_3$ moiety is oriented almost parallel to the surface normal, similar to SAM^O on Ag (Figure 1b). For SAM^O on Au, the terminal moiety is oriented away from the surface normal, analogous to SAM^E on Ag (Figure 1b). This reversal in orientation of the terminal moiety across the substrates is understood to be due to a change in hybridization at the headgroup from a S_{sp^3} to a S_{sp}.[9,41,43] We therefore hypothesized that a change in the orientation of the terminal moiety, as a result of a change in the substrate, will lead to a reversal in γ, which leads to an inversion of the odd−even effect; i.e., on Ag^{TS}, SAM^O would have higher contact angles than SAM^E, while the reverse was true with Au^{TS} SAMs.

Inverting Orientation of Surface Moiety Inverts the Odd−Even Effect in Hydrophobicity. Figure 3 shows our results with Ag substrates. We prepared Ag^{TS} and Ag^{AD} surfaces that showed a significant difference in roughness (rms of 0.6 ± 0.04 and 5.1 ± 0.2 nm, respectively). The observed roughness data are comparable to those previously observed by others.[37,38] As previously observed, template-stripped surfaces, Ag^{TS}, had larger grains and smaller asperities than the "as-deposited", Ag^{AD}, surfaces.[36] We, however, observe that there is a slight difference in the rms roughness between the two metal surfaces, irrespective of the method of preparation. The M^{AD} surfaces were the roughest and showed the largest differences (rms $|Ag^{AD} - Au^{AD}| = 2.86$ nm), while M^{TS} surfaces showed a slight variation (rms $|Ag^{TS} - Au^{TS}| = 0.24$ nm). Despite the small difference in roughness between the M^{TS}, we believe that comparison of hydrophobicity of SAMs formed on these surfaces will give general insights into monolayers because the differences in roughness are in the order of 1.5 C−C bond length, a defect that can be mitigated by gauche effects during the assembly process. Table 1 lists the average of θ_s for all SAMs on the two metal substrates from at least seven measurements per sample.

As observed with Au surfaces, measurements of water θ_s showed an odd−even effect in Ag^{TS} but not in Ag^{AD}. When the surface is changed from Au to Ag, the odd−even effect inverts; SAM^O has a higher θ_s than SAM^E. As predicted, the odd−even effect has inverted with the change of substrate analogous to inversion in the orientation of the terminal moiety and, hence, the surface dipole. On the basis of our data, we infer that the previously reported odd−even effect in hydrophobicity of Ag SAMs was inaccurate for three reasons: (i) the differences in values of contact angles between the odds and evens for medium-sized SAMs were not subjected to any statistical test for significant differences at any confidence interval; (ii) the zigzag oscillation is analogous to what we observe in Au, suggesting that the oscillation could be due to an artifact, as previously suggested by Whitesides and co-workers,[20] or an overinterpretation of the data; and (iii) with the as-deposited surface, M^{AD}, we did not observe an odd−even effect even after repeated measurements. From the rms roughness of the Ag^{AD} surfaces, the asperities are too large to allow for formation of a well-defined interface upon formation of the monolayer. We, therefore, concur with Whitesides and co-workers[20] that the odd−even effect reported by Porter and co-workers[14] could be due to surface oxidation or adventitious impurities.

To understand the origin of the difference in SAM^O and SAM^E and, hence, the odd−even effect, we examined the difference in θ_s for SAMs with similar terminal group orientation (Ag odds versus Au evens and Ag evens versus Au odds) and compared these differences to SAMs whose terminal groups are oriented differently (Ag odds versus Au odds and Au evens versus Ag evens). Figure 4 gives the values

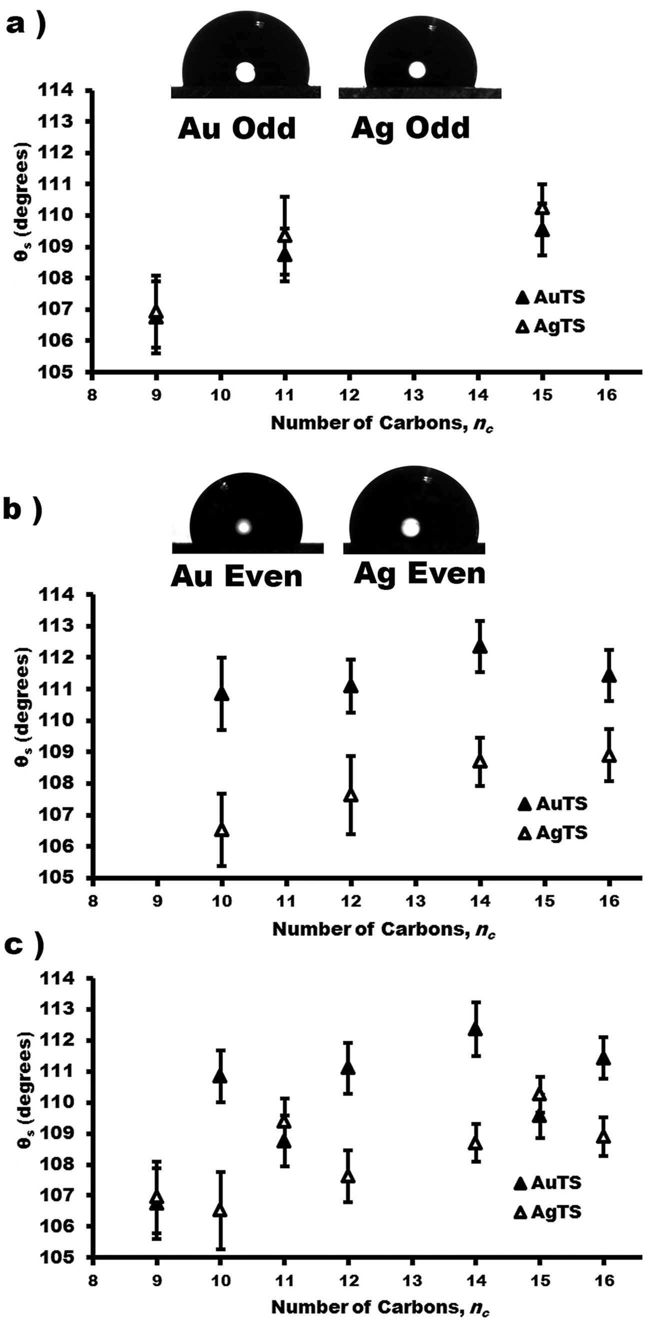

Figure 4. Comparison of the hydrophobicity of odd and even *n*-alkanethiolates SAMs on Ag^{TS} and Au^{TS} surfaces shows an additive (SAM^E) and subtractive (SAM^O) coupling of two effects that dominate hydrophobicity of the SAM. (a) Static contact angles, θ_s, of SAM^O on Ag^{TS} and Au^{TS} show no statistically significant difference ($p > 0.1$). The insets show 5 μL droplets of DI water on a C_9 SAM on either Au or Ag. (b) Similarly, θ_s from SAM^E shows a significant difference in the values of θ_s ($p < 0.01$). The insets show 5 μL droplets of DI water on a C_{10} SAM. (c) All values of θ_s derived from both surfaces over the two series of thiols. The difference in the contact angles allow us to decouple the effect of the packing density from surface dipoles and illustrate which one dominates in SAM hydrophobicity.

of θ_s for SAM^O (Figure 4a) and SAM^E (Figure 4b) and a summary of all of the data (Figure 4c). We observe that contact angles derived from SAM^O are statistically indistinguishable (average $|\Delta Au_{odd} - Ag_{odd}| \approx 1°$; Student's *t* test, $p > 0.1$). The small difference in θ_s indicates that its origin has a minor or no effect on the wetting properties of the SAMs. For SAM^E, however, we observed a statistically significant difference ($p < 0.01$) in the values of θ_s (average $|\Delta Au_{even} - Ag_{even}| \approx 5°$).

Surface Dipole versus Packing Density. The difference between SAM^E on both substrates showed the largest difference, suggesting that this difference probably captured all factors contributing to the odd−even effect in hydrophobicity of SAMs; i.e., this is a result of an additive effect, while the small difference in SAM^O is due to a subtractive effect. We hypothesized that the packing density and surface dipole, because of orientation of the terminal moiety, could account for the origin of the odd−even effect because there were no major stereoelectronic perturbations upon *n*-alkanethiols binding on the metal surface[26] to influence surface properties. Considering SAMs with similar orientation of the terminal moiety, there is a ~2° difference in θ_s; that is, average $|\Delta Au_{odd} - Ag_{even}|$ = average $|\Delta Au_{even} - Ag_{odd}| \approx 2°$). Because the molecular moieties on the surfaces are the same for these pairs of SAMs, one can argue that 2° is due to the difference in the packing density. Considering hypothetical SAM^E and SAM^O with equal length on both substrate, the differences in values of θ_s between this pair of SAMs was calculated to be ~3°. Because the orientation of the surface moiety and, hence, dipole moments change upon substituting Ag with Au, we argue that the effect of the orientation of the surface moiety is ~3°, which is slightly larger than the influence of the packing density. We can therefore conclude that the odd−even effect in hydrophobicity is more influenced by the orientation of the surface moiety or surface dipoles[26] than the packing density. Others have also observed differences in monolayer properties because of orientation of the terminal moiety.[1,2,44]

The increase in packing density with the change of substrate from Au to Ag should make the SAM interface with water more polyethylene-like, especially for SAM^E. Figure 4b shows that values of θ_s are lower for Ag^{TS} than those on Au^{TS}. This indicates a decrease in hydrophobicity and a trend toward the contact angle of polyethylene (88−103°).[40,45] A decrease in θ_s because of an increase in packing density (tending to polyethylene-like structure), however, would be mitigated by a more dominant effect if such an effect exists in these SAMs. The decrease in θ_s for SAM^E occurs alongside changes in the orientation of the surface moiety, hence, surface dipole, from being along the surface normal to being tilted away from the surface normal. An analogous change, albeit in the reverse order, occurs with SAM^O, and as such, by comparing θ_s for SAM^O on Au and Ag, we generate a set of elementary simultaneous equations (from SAM^E, $a + b = 5°$, and from SAM^O, $a - b = 1°$), the solutions of which give us the contribution as a result of the packing density ($b = 2°$) and effect of the surface dipole ($a = 3°$). The surface dipole is therefore a more dominant effect than the change in the packing density (see Figure S1 of the Supporting Information). The effect of surface dipoles on wettability with polar liquids has previously been shown to follow a similar trend; that is, an increase in surface dipoles leads to an increase in θ_s.[22,24,31] This paper highlights two key points relating to hydrophobicity that can be translated to wetting and other technologies relying on liquid contact with a SAM: (i) Experimental realization of the odd−even effect in wetting, here, hydrophobicity, depends upon the quality of the surface. (ii) Surface dipoles has a more dominant effect than the packing density in SAM hydrophobicity and may account for the high θ_s, relative to hydrocarbon polymers. This paper also serves to clarify the apparent ambiguity in literature data regarding hydrophobicity of SAMs.

■ ASSOCIATED CONTENT

Supporting Information

Materials and methods, schematic illustration of the effects of the packing density and change in orientation of the surface moiety on the hydrophobicity of SAMs (Figure S1), and sample images from each SAM that we measured (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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